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## An Alternative Indicator for the Collapse Transition: Autocorrelation Time

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### Abstract

In canonical statistical analysis, it is common to employ response quantities such as the specific heat to identify changes in the thermodynamic behavior of finite systems. However, as a consequence of finite-size effects, conventional thermodynamic quantities do not necessarily exhibit clear indications for pronounced thermal activity. By means of Metropolis Monte Carlo simulations of a coarse-grained model for flexible polymers, we investigate how the integrated autocorrelation times of energetic and structural quantities depend on the temperature. We show that, due to critical slowing down, an extremal autocorrelation time can also be considered as an indicator for the so-called collapse transition, which corresponds to a gas-liquid phase transition.

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### 1. Instruction

The biological function of proteins is often related to their three-dimensional geometric structures and severe illnesses can be caused by the misfoldings of proteins. Therefore, the necessity for a better understanding of general physical principles and mechanisms of structural transitions of polymers such as folding, crystallization, aggregation, and the adsorption at solid and soft substrates has increased rapidly in the past decades. Experimental and computational approaches have been developed to understand these various features. In order to improve the statistical accuracy of estimated expectation values of measured physical quantities, appropriate estimates of the corresponding autocorrelation times are necessary. In the past, most of the studies on analyzing the properties of the autocorrelation times focused on spin models. In the Ising model, the phase transition between ferromagnetism and paramagnetism is of second order. In the thermodynamic limit (i.e., infinite system size), the autocorrelation time  $\tau$  approximately satisfies the power law  $\tau \propto \xi^z \propto |1 - T/T_c|^{-\nu z}$  in the neighborhood of the critical point  $T_c$ , where  $\xi$  denotes the spatial correlation length,  $\nu$  and  $z$  denote the critical exponent and dynamic critical exponent, respectively. In computer simulation,  $z$  is an algorithm dependent critical exponent. For a system with finite size  $L$ ,  $\tau \sim L^z$  at temperatures

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sufficiently close to the critical point [Landau and Binder (2000); Newman and Barkema (1999); Janke (2002)]. The combination of local updates, such as single spin flips, and the Metropolis algorithm [Metropolis et al. (1953)] cause the autocorrelation time to be rather large, since  $z \approx 2$  in this case. This effect is usually called critical slowing down which can be reduced to less than unity if non-local update mechanisms, such as Swendsen-Wang, Wolff, and multigrid algorithms are employed [Newman and Barkema (1999); Janke (1998); Sokal (1989, 1992); Kandel et al. (1988, 1989); Coddington (1992)]. For systems exhibiting a first-order phase transition, the dynamics in a canonical ensemble will suffer from the “supercritical slowing down”. At the transition temperature, the average residence time the system spends in a pure phase is described by the autocorrelation time  $\tau \propto \exp(2\sigma L^{d-1})$ , where  $\sigma$  is the (reduced) interface tension and  $L$  is the projected area of the interfaces. For our study, we investigated the autocorrelation times of different quantities for a coarse-grained, elastic, flexible polymer model with the combination of local monomer displacement and Metropolis Monte Carlo sampling. The reason why we chose this combination is to resemble Brownian dynamics in a canonical ensemble. Our goal is to identify structural transitions and transition temperatures by employing autocorrelation times.

## 2. Model and Methods

We employ a model for elastic and flexible homopolymers [Bachmann (2014)], where the bonds are represented by the finitely extensible nonlinear elastic (FENE) potential [Bird et al. (1987); Kremer and Grest (1990); Milchev et al. (2001)]

$$V_{\text{FENE}}(r_{ii+1}) = -\frac{K}{2} R^2 \ln \left[ 1 - \left( \frac{r_{ii+1} - r_0}{R} \right)^2 \right]. \quad (1)$$

Non-bonded monomers interact via a truncated, shifted Lennard-Jones potential

$$V_{\text{LJ}}^{\text{mod}}(r_{ij}) = V_{\text{LJ}}(r_{ij}) - V_{\text{LJ}}(r_c). \quad (2)$$

with

$$V_{\text{LJ}}(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right], \quad (3)$$

The total energy of a conformation  $\zeta = (\vec{r}_1, \dots, \vec{r}_L)$  for a chain with  $L$  monomers reads

$$E(\zeta) = \sum_{i=1}^{L-2} \sum_{j=i+2}^L V_{\text{LJ}}^{\text{mod}}(r_{ij}) + \sum_{i=1}^{L-1} V_{\text{FENE}}(r_{ii+1}). \quad (4)$$

Details of the parametrization are given in Qi and Bachmann (2014).

We employed the Metropolis Monte Carlo Method combined with local displacement updates in our simulation. In a single MC update, the conformation is changed by a random local displacement of a monomer. A chosen monomer is allowed to change its position within a small cubic box with edge lengths  $d = 0.3r_0$ . Once the update is suggested, we further utilize the Metropolis criterion [Metropolis et al. (1953)],

$$p = \min(1, \exp[-\beta(E_{\text{new}} - E_{\text{old}})]), \quad (5)$$

to decide if the update is accepted. Here, the inverse thermal energy is denoted by  $\beta = 1/k_B T$  (we set  $k_B \equiv 1$  in the simulations);  $E_{\text{old}}$  and  $E_{\text{new}}$  are the energies before and after the proposed update, respectively.

Suppose we generate a time series with a large number of data  $N$  from an importance sampling MC simulation. For a quantity  $O$ , the strength of the correlation between two measurements with time displacement  $k$  is described by the autocorrelation function

$$A(k) = \frac{\langle O_l O_{l+k} \rangle - \langle O_l \rangle^2}{\sigma_O^2}, \quad (6)$$

where  $l$  can be any integer in the range  $[1, N - k]$ , and  $\sigma_O^2 = \langle O_l^2 \rangle - \langle O_l \rangle^2 = \langle O^2 \rangle - \langle O \rangle^2$  is the standard variance of  $O$ . As usual, the autocorrelation function is a monotonically decreasing function. The independence of two measurements

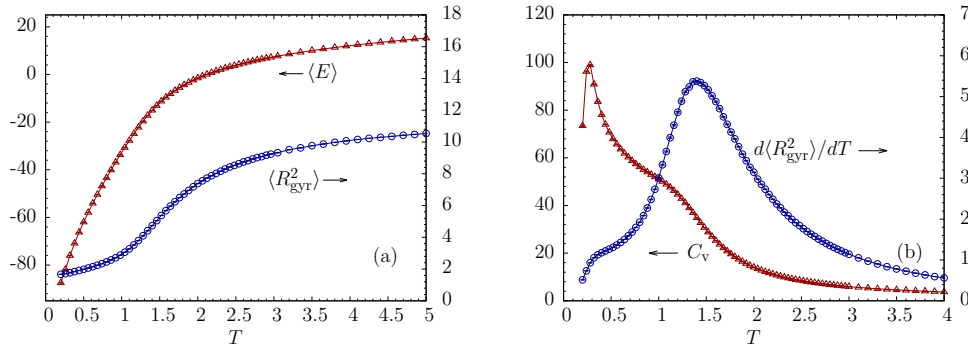


Fig. 1. (a) Mean energy  $\langle E \rangle$  and square radius of gyration  $\langle R_{\text{gyr}}^2 \rangle$ ; (b) heat capacity  $C_v$  and thermal fluctuation of the square radius of gyration  $d\langle R_{\text{gyr}}^2 \rangle/dT$  for a flexible polymer with 30 monomers. Error bars are smaller than the symbol size.

is judged by the autocorrelation time  $\tau$ . If the time displacement between two measurements is larger than  $\tau$ , these two measurements are considered to be independent. For large time separation  $k$ , the autocorrelation function decays exponentially,

$$A(k) \longrightarrow e^{-k/\tau_{O,\text{exp}}}, \quad (7)$$

where  $\tau_{O,\text{exp}}$  is the exponential autocorrelation time of  $O$ . Because of large statistical fluctuations in the tail of  $A(k)$ , the accurate estimation of  $\tau_{O,\text{exp}}$  is often difficult. Instead, we can calculate the integrated autocorrelation time

$$\tau_{O,\text{int}} = \frac{1}{2} + \sum_{k=1}^N A(k), \quad (8)$$

which can be obtained by

$$\tilde{\tau}_{O,\text{int}}(k_{\text{max}}) = \frac{1}{2} + \sum_{k=1}^{k_{\text{max}}} \tilde{A}(k), \quad (9)$$

where  $\tilde{A}(k)$  is the estimator of  $A(k)$  and  $k_{\text{max}}$  is the maximum time displacement. Because of Eq. (7),  $\tilde{\tau}_{O,\text{int}}$  will finally converge to a constant [Janke (2002)]. An alternative way of calculating the integrated autocorrelation time is by binning analysis [Janke (2002); Bachmann (2014)], in which case the integrated autocorrelation time is estimated by

$$\tilde{\tau}_{O,\text{bin}} = \frac{1}{2} N_B \frac{\tilde{\sigma}_{\tilde{O}^B, c}^2}{\tilde{\sigma}_O^2}, \quad (10)$$

where  $N_B$  is the bin size,  $\tilde{\sigma}_{\tilde{O}^B, c}^2$  denotes the estimator for the variance of the binning block averages, and  $\tilde{\sigma}_O^2$  is the estimator for the variance of  $O$  [Qi and Bachmann (2014)]. As  $N_B$  increases, this estimator will converge to a constant which corresponds to integrated autocorrelation time. This method is more convenient than the integration method (Eq. (9)) since a precise estimate of the autocorrelation function is not needed.

### 3. Results

We first investigate two representative quantities by means of canonical analysis. The statistical averages of energy and square radius of gyration are shown in Fig. 1(a) and their thermal fluctuations are plotted in Fig. 1(b). At high temperatures, due to large thermal fluctuations, the polymer is in the gas phase and dominant structures are dissolved or random coils. As temperature decreases, the polymer collapses, and compact globular conformations (liquid phase) are favorably formed. A clear collapse transition signal is exhibited in the thermal fluctuation of the square radius of

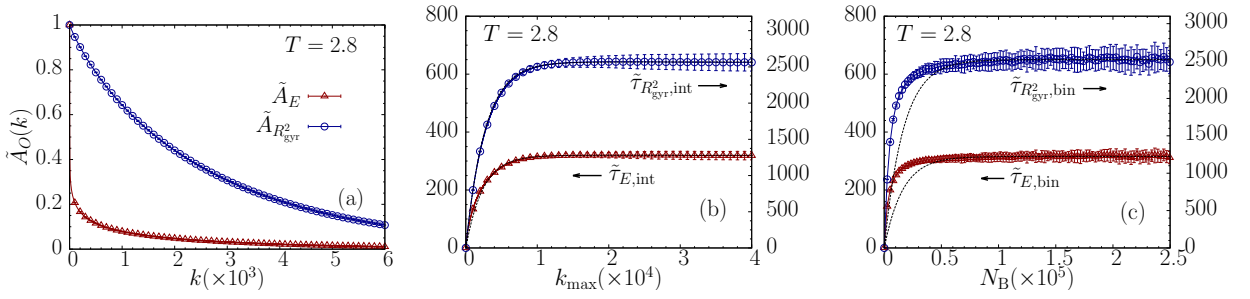


Fig. 2. (a) Autocorrelation functions of  $E$  and  $R_{\text{gyr}}^2$  at  $T = 2.8$  for the 30-mer. For each quantity, the estimated integrated autocorrelation time converges to a constant as shown in (b). The corresponding binning analysis results also show good convergence and are plotted in (c). Dashed lines represent the fitted curves.

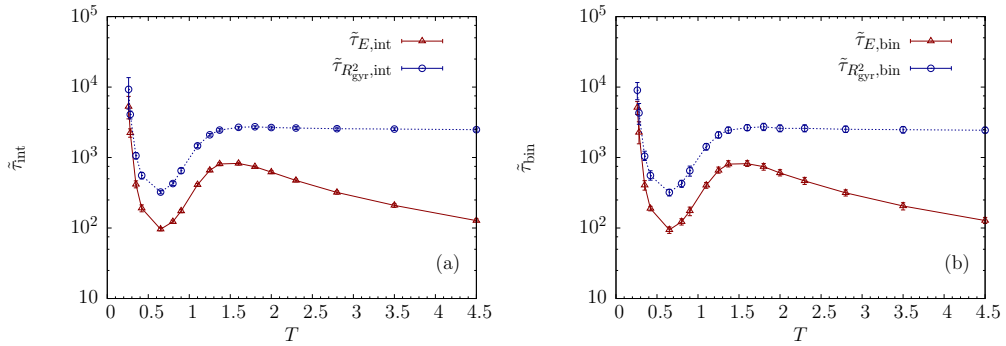


Fig. 3. Temperature dependence of integrated autocorrelation times (a) obtained by the integration of autocorrelation functions; (b) estimated with the binning method for the 30-mer.

gyration curve where a peak occurs at  $T \approx 1.4$ , whereas the heat capacity curve only presents a “shoulder” around this temperature. As the temperature decreases further, the polymer transfers from the globular phase to the “solid” phase which is characterized by locally crystalline or amorphous metastable structures. A corresponding transition peak could be observed in the heat capacity curve where the freezing transition happens at  $T \approx 0.28$ .

We performed the integration of the autocorrelation (8) and the binning analysis to estimate the integrated autocorrelation times at 17 temperatures in the interval  $T \in [0.26, 4.5]$  for the 30-mer. Once we generated the estimated integrated autocorrelation time curves for these two methods in each temperature [details of the procedures that we employed to generate these two curves are given in Qi and Bachmann (2014)], we further performed least square fitting for these curves in order to estimate the integrated autocorrelation time systematically. The empirical fit function for any quantity  $O$  is chosen to be of the form

$$f_O(x) = \tau_O^f (1 - e^{-x/x^f}), \quad (11)$$

where  $x$  represents  $k_{\text{max}}$  in the integration of the autocorrelation functions method and  $N_B$  in binning analysis;  $\tau_O^f$  and  $x^f$  are two fit parameters. An example containing the estimated integrated autocorrelation time curves and the corresponding fitting curves are plotted in Fig. 2.

Figure 3 shows how the fitted estimated integrated autocorrelation times  $\tau_O^f$  vary with temperature. In Fig. 3(a) the integrated autocorrelation time curves, estimated by using integration method, are shown. These results are virtually identical to the ones estimated by binning analysis [see the Fig. 3(b)]. The integrated autocorrelation time of  $R_{\text{gyr}}^2$  is always larger than that of  $E$ . This is because the structural quantity is less sensitive to conformational changes within a single phase and the displacement update does not allow immediate substantial changes. Slowing down occurs at  $T \approx 1.4$  in the autocorrelation time curves. Comparing with the collapse transition signals in Fig. 1(b) near this

temperature leads to the claim that slowing down can also be used as an indicator to locate the  $\theta$  transition temperature. Within this temperature region, the autocorrelation time becomes extremal. Large parts of the polymer have to behave cooperatively which delays the overall collapse dynamics. In the low temperature region, autocorrelation times of all quantities begin to increase considerably. The autocorrelation time calculation is ceased at  $T < 0.26$  for the reason that Metropolis simulation with local updates typically get stuck in metastable states of polymer at low temperatures. In addition, the autocorrelation times naturally increase at low temperatures, because of low entropy. Therefore, the freezing transition is not easily accessible using the autocorrelation analysis. Last but not least, the autocorrelation times of  $R_{\text{gyr}}^2$  converge to a constant value as temperature increases but the one of  $E$  decays. One partial reason is that  $R_{\text{gyr}}^2$  possesses upper limiting values at high temperatures whereas  $E$  could access any value in the continuous model.

#### 4. Summary

We have investigated the autocorrelation time properties for different quantities by employing the Metropolis Monte Carlo algorithm for a simple coarse-grained flexible polymer model. We estimated the autocorrelation times for various temperatures and performed an autocorrelation analysis by using the integration method and binning analysis. The primary result is that slowing down occurs as expected and is clearly represented by peaks in the autocorrelation time estimators near the collapse transition temperature. By comparing with temperatures of extremal thermal structural fluctuations, we claim that the extremal autocorrelation time can also be considered as an indicator for the collapse transition.

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